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THE EFFECT OF A PROTECTIVE GAS ATMOSPHERE ON THE REDUCING POTENTIAL OF THE MELT TANK

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A method is considered that makes it possible to reduce tin oxides in the low-temperature zone of the melt tank, where they are predominantly formed. Based on the experimental data, a linear equation of multiple regression is obtained describing the effect of the protective gas medium on the reducing potential of the melt tank.

Sheet glass in Russia, like in other countries, is mostly produced by the high-technology float method.

To obtain glass with good service parameters, certain physicochemical conditions should be developed for glass formation, namely a non-oxidizing medium in the melt tank For this purpose a nitrogen-hydrogen mixture is constantly supplied into the float-glass tank. The most common method at present is based on differentiated feed of hydrogen into the melt tank. This is due to the fact that with decreasing temperature the reducing capacity of hydrogen markedly decreases, and in order to prevent oxidation of tin or reduction of the forming oxides, it is important (especially in the low-temperature tail part of the melt tank) to maintain an increased concentration of hydrogen.

The quantity of protective gas mixture supplied into the melt tank and the regulation of the gas currents are important for maintaining the optimum physicochemical conditions of the float glass production. The quantity of protective mixture supplied to the tank should provide for a high frequency of its exchange (the protective gas mixture inside the melt tank should be completely renewed every 3 – 3.5 min). It is advisable to implement the maximum feed of the mixture between the middle and head parts of the melting tank in order to ensure the release of the major part of the evaporation and reaction products, such as tin sulfides, tin oxides, metallic tin vapors, hydrogen sulfide, and water vapor via the inlet and outlet technological openings of the melting tank, preventing the condensation of these compounds on the surface of the equipment or the glass band. Barriers inside the gas space are widely used to regulate the gas flows in the melting tank.

The use of the specified traditional methods is not always capable of ensuring the required physicochemical conditions of glass band formation and preventing the formation of tin oxides in the low-temperature zone of the melting tank, which leads to the formation of defects in the glass. This is due to the fact that the oxygen-containing compounds that oxidize the molten tin inevitably penetrate into the melt tank, first, from the ambient air during short-term depressurization of the tank (for instance, during replacement of the peepholes or rearrangement of the equipment), second, released from the glass melt during its discharge onto the tin melt and spreading, and third, penetrating into the tank with the protective mixture, since they are inevitably present in this mixture. Therefore, various additives [1] are introduced into the protective gas mixture in order to increase its reducing potential.

The practice of float-glass production lines shows that the majority of tin oxides are formed in the tail part of the melting tank (in the temperature zone of 600 – 700°C). However, reduction of tin oxide by oxygen is possible only at a temperature above 700°C, since the reducing potential of hydrogen below the specified temperature is virtually equal to zero. Therefore, tin oxide is permanently present near the outlet opening of the tank and has to be mechanically removed, since otherwise tin oxide sticks to the bottom surface of the glass band, which is classified as a defect.

The Saratov Institute of Glass has developed a method that allows for effective reduction of tin oxides in the tail (low-temperature) part of the tank, where these oxides are predominantly formed. The method implies introduction of a certain concentration of carbon monoxide CO together with the reducing gas (hydrogen) in the protective gas mixture supplied to the low-temperature part of the melting tank. As distinct from hydrogen, carbon monoxide is capable of reducing tin oxides starting at a temperature of 450°C. It should be noted that one of the factors motivating the selection of carbon monoxide as an additive is the fact that it is a side impurity in the protective atmosphere resulting from in-

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complete high-temperature combustion of natural gas mixed with air [2, 3].

When carbon monoxide was introduced into the low-temperature zone of the melt tank on the ÉPKS-4000 line at the Saratov Institute of Glass, the glass defects caused by tin oxide sticking to the bottom surface of the glass decreased. It should be noted that this occurred under an extended service period of the float tank, when the regulated physicochemical parameters of the molding process have accordingly deteriorated.

Since the formation of tin oxides in the low-temperature zone of the melt tank and, accordingly, the glass defects caused by tin oxide sticking to the bottom surface are determined by a multi-factor dependence of the set of physicochemical molding parameters, statistical processing of data was used to achieve an objective evaluation of the effect of the proposed method [4, 5]. A linear equation of multiple regression was taken as a mathematical model of this process:

$$Y = b_0 + b_1 X_1 + b_2 X_2 + \ldots + b_n X_n ,$$

where Y is the glass defect caused by tin oxide sticking to the bottom surface of glass in 12 h of operation of the ÉPKS-4000 line, m^2; b_i are constants ($i = 1, ..., n$); X_1 is the volume content of carbon monoxide in the protective gas mixture supplied to the tail part of the melt tank (carbon monoxide is introduced into the protective mixture to raise its reducing potential), %; X_2 is the volume content of carbon monoxide in the gas space of the low-temperature zone of the melt tank (to effectively use the carbon monoxide as an additive introduced into the protective medium, the CO content in the protective medium supplied ought to be higher than the CO content in the gas space of the melt tank; when this condition is satisfied, it shows that carbon monoxide is spent on reducing the tin oxides formed in the low-temperature part of the melt tank), %; X_3 is the volume content of hydrogen in the protective mixture supplied to the tail part of the melt tank (the presence of a reducing gas, i.e., hydrogen in the protective mixture, is the traditional method for preventing the oxidation of tin and reduction of the tin oxides formed in the melt tank), %; X_4 is the volume content of hydrogen in the gas space of the low-temperature tank zone (a protective medium containing hydrogen as a reducing component is incapable of reducing tin oxides in this zone; however, due to the high frequency of renewal of the protective medium in the melt tank, it can prevent the formation of tin oxides), %; X_5 is the volume content of moisture impurities (H2O) in the protective medium supplied to the tail part of the melt tank (moisture in small quantities is inevitably present in the protective mixture, since the latter is not amenable to complete adsorption purification from water vapor), %; X_6 is the volume content of moisture impurities (H_2O) in the gas space of the low-temperature zone of the melt tank (as the probability of tin oxidation by water vapor is higher in the tail part of the melt tank than in the front part, it is necessary to know the amount of moisture penetrating into the tank with the protective atmosphere X_5 and the content of moisture in the gas medium of the tank; if the gas space of the melt tank contains more moisture than the protective atmosphere supplied to the tank, the moisture is formed inside the melt tank according to the reaction between oxygen and hydrogen $\{H_2\} + \{O_2\} \rightarrow \{H_2O\}$ due to inadequate sealing of the tank), %; X_7 is the thickness of the glass produced (the thickness of the glass affects the temperature in the tail part of the melt tank and the molding rate, which determines the intensity of the tin flows in the tail part of the tank entraining the surface tin oxides underneath the glass band), mm; X_8 is the quantity of the protective mixture supplied into the melt tank (this quantity determines the frequency of exchange of the protective medium in the melt tank), m^3/h.

It should be noted that the content of oxygen in a protective medium is an important parameter. This is due to the fact that tin oxidation is possible within the whole temperature range of the melt tank even when infinitely small quantities of oxygen are present in the protective medium of the tank. The most dangerous is the low-temperature zone (600°C), in which 2×10^{-22} vol.% oxygen is sufficient for the oxidation reactions, which is 14 orders of magnitude lower than the quantity required for these reactions in the front zone.

However, in our case, a stable content of oxygen was observed in the protective medium supplied and in the gas space of the low-temperature zone of the melt tank; therefore, we did not consider it for the multiple regression equation at the first stage of our studies.

The coefficients in the multiple regression equations were estimated on the basis of experimental data using the Statgraf program. Assuming that the dependence of the glass defect caused by tin oxide adhesion Y depending on X_1, ..., X_8 is linear, the following parameters with a probability of 0.95 have an effect on Y (the extent of the effect is estimated based on their significance level, which was determined as well using the Statgraf program): X_7 — the molded glass thickness, X_2 — the carbon monoxide content in the gas space of the low-temperature zone of the melt tank, and X_4 — the hydrogen content in the gas space of the low-temperature zone of the melt tank.

The other parameters also affect the glass defect caused by tin oxide adhesion but their effect cannot be estimated by a linear dependence. Therefore, the work of selecting a particular dependence for each parameter will be continued, i.e., the regression equation will represent a linear combination of certain preset functions (they can be, for instance, polynomials of any power, exponential or trigonometric functions, etc.).

The following linear equation of multiple equation was obtained:

$$Y = 37.2 - 98.0X_2 + 7.1X_4 - 3.5X_7 ,$$

Thus, the defect in glass caused by tin oxide adhesion depends on:

– the thickness of the float glass produced on the line: the smaller the glass thickness, the more substantial the defects

(thin glass is produced with a high drawing speed, which creates intense tin flows in the melt facilitating the entrainment of the tin oxides formed in the tail part of the tank underneath the glass band);

– the content of the reducing gases, i.e., carbon monoxide and hydrogen, in the gas space of the low-temperature zone of the melt tank.

According to the multiple regression equation, the defect caused by sticking tin oxide for a glass thickness of 5 mm and a content of the reducing gas (hydrogen) in the gas space of the low-temperature tank zone equal to 5 vol.% amounts to 55.2 m^2 of glass in 12 h of the float line operation. For a 5% volume content of hydrogen and 0.25% carbon monoxide impurity in the gas space of the tail part of the tank, the defect caused by tin oxide adhesion will decrease by 44.4% and amount to 30.7 m^2 of glass.

The obtained linear equation of multiple regression confirms the efficiency of the developed method according to which combined gas media containing a large quantity of hydrogen with a small carbon monoxide additive can be effectively used to increase the reducing potential of the melt tank.

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